EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Aqueous solvation dynamics monitored by sub-nanosecond time-resolved Wide Angle X-ray Scattering and X-ray Absorption Spectroscopy**	**Experiment number**: CH-6004
Beamline:	**Date of experiment**: from: 17 November 2021 to: 23 November 2021	**Date of report**: **10.12.2021**
Shifts:	**Local contact(s)**: Matteo Levantino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

This exeriment aimed to study the generation and fate of photogenerated halogen radicals in aqueous solution. For this we investigated the subsequent kinetics following i) photodetachment from aqueous iodide generating nascent iodine atoms, and ii) after photoexcitation of aqueous tri-iodide. The tri-iodide experiment aimed to help assign the subsequent reaction products in the iodide detachment experiments.

In the iodide detachment experiment, after the sub-picosecond solvent reorganization, we monitored geminate recombination and secondary reaction product formation. Our measurements concentrated on 400 nm multi-photon driven electron ejection from aqueous halogen anion(s), mainly I^-, and to a lesser extent Br^-(aq). This approach allowed us to identify the structural signals around the nascent halogen atom(s) X^0 (X = I, Br), and to follow the formation of secondary species, I_2^-, I_3^- etc [1], which we probed with ~ 100 ps time-resolved Wide-Angle X-ray Scattering (WAXS). Molecular Dynamics (MD) simulations hint towards different solvation shell structures around the nascent halogens I^0(aq) and Br^0(aq) [1], exhibiting different mean X^0-OH_2 distances. One goal was to extract a detailed picture of the equilibrated water cage structure around the atomic halogen atoms. Observing the formation kinetics of the secondary species is important as these species influence the geminate X^0-e^- recombination kinetics which have been interpreted in laser-oinly measurements as being due to the formation of an X^0-e^-(aq) contact pair [1,2].

In the control experiment we investigated the quasi reverse process, 400 nm photodissociation of triiodide (I_3^-), which initially yield ($I_2^- + I^0$) [3]. The WAXS measurements can detect any intermediates or products of this dissociation reaction [3].

The samples were prepared by dissolving NaBr and NaI salts in concentrations of 10 mM – 1 M in deionized water. Triiodide was generated by mixing iodine (I_2) and iodide (I^-) in water. Sample solutions were delivered into the interaction region via a closed loop liquid flat sheet jet of 300 μm thickness. 400 nm laser pulses (with ~ 1 ps FWHM, round spot of 300 μm, 1 kHz, with up to ~ 400 mJ/cm^2) was generated by second harmonic

generation from the Ti:Sapphire amplifier and used for multi-photon ionization of the halides and for photodissociation of triiodide. The optical laser and x-ray beams overlapped spatially and temporally at the sample position with the X-ray beam (100 (H) x 60 (V) μm^2). The laser intensity was varied between 55 and ~ 550 µJ. Pink beam X-rays at ~ 18 keV were scattered from the samples over a helium purged chamber into the Rayonix MX170-HS CCD detector at varying time-delays from -3 ns to 1 µs and with a resolution of ~ 100 ps around time zero. The detector covered the q-space of up to ~ 8 $Å^{-1}$ at 18 keV.

The transient WAXS at different time delays were produced from pairs of azimuthally integrated laser on and laser-off WAXS images (Figs. 1 and 2). Additionally, the solvent (water) scattering response to the laser heating was obtained in a separate measurement under the same conditions using a special dye (not shown). WAXS patterns were recorded for various time delays in the -3 ns to +1 µs region (~ 15 time points, each scan). Our time-resolved WAXS spectra after electron photo-detachment from aqueous iodide (Fig. 1) clearly show the pronounced transient laser-induced water heating signal (~ 1.5-3 $Å^{-1}$), the change in the local water shell around the nascent iodine atom (q < 1 $Å^{-1}$) next to the generation of the reaction products I^0, I_2^-, (e.g., q > 3 $Å^{-1}$). Both the signal below 1 $Å^{-1}$ and above ~ 3 $Å^{-1}$ change on a 1 ns time scale, most likely due to the formation of I_2^-, I_3^- (analysis underway). The time-resolved WAXS spectra of triiodide also shows interesting changes especially in the q-ranges < 1 $Å^{-1}$ and > 3 $Å^{-1}$, which has not bee reported previously [3]. The analysis of both groups of samples containing the same species in different charge states (I, I_2 and I_3) should allow us to unambiguously unravel the subnanosecond and submicrosecond reaction products. This will allow a more quantitative analysis of the iodine atom survival, which will allow us to confirm or falsify the existence od a long-lived aqueous contact pair (I-e).
All WAXS measurements were recorded for different laser pulse energies (to match sample excitation conditions for different solute concentrations). Reaction product formation was also studied as a function of the initial solute concentration.
Overall, this experiment was successful and we were able to complete the entire measurement program within the allocated beamtime. Beamline ID09-TR is extremely well suited for time-resolved measurements, we are most grateful to the tremendous support we received in both setup, experiment execution, and analysis from Matteo Levantino (beamline responsible), but also Michael Wulff next to the superb beam delivery by the ESRF machine group.

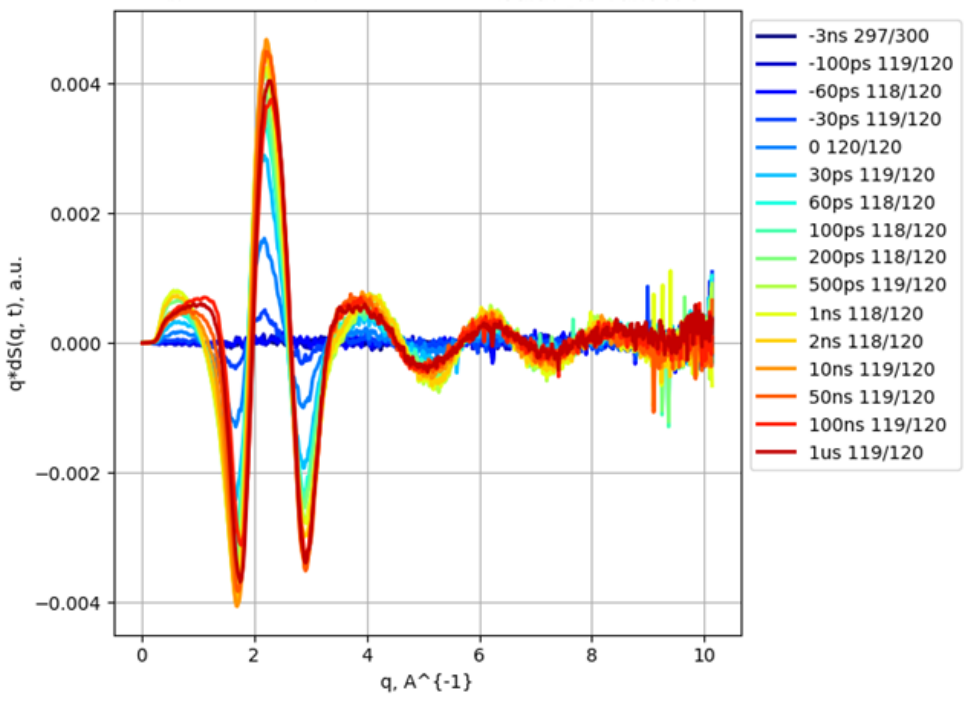

Fig. 1: Exemplary transient WAXS signal recorded after 400 nm photoexcitation of aqueous I^- produced from pairs of azimuthally integrated laser on and laser-off images. The different time delays are color coded, the x-axis displays the scattering vector q, while the y-axis displays the intensity of the signal.

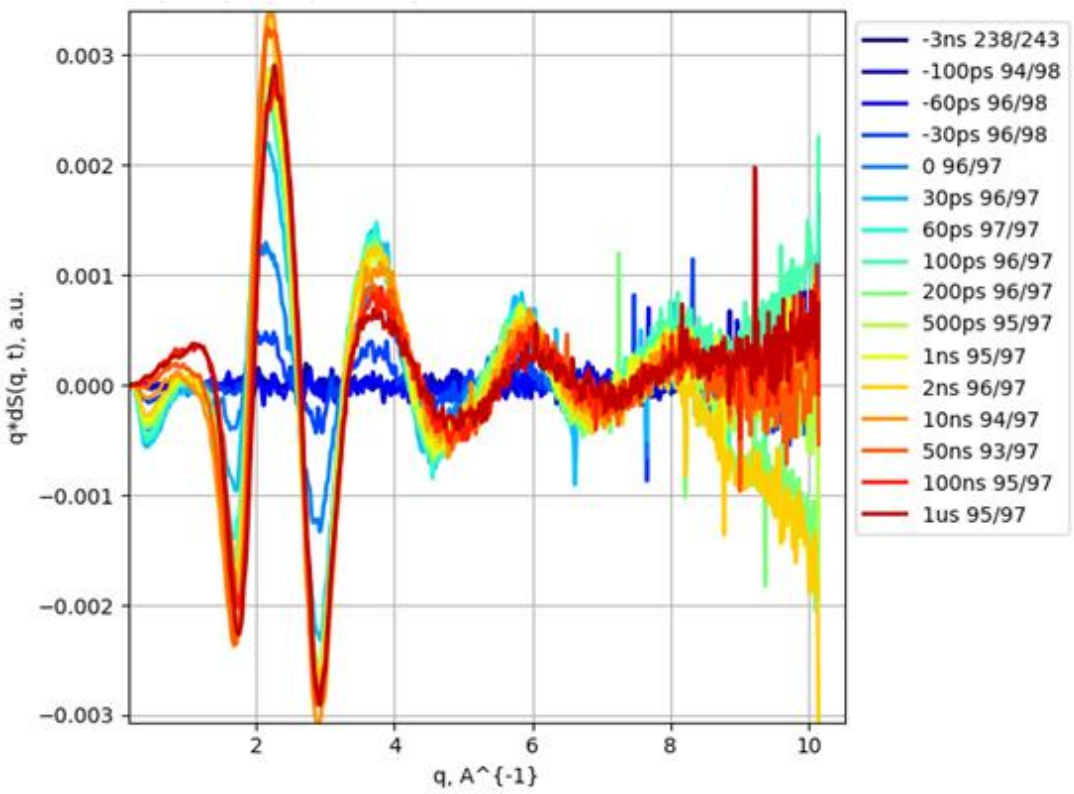

Fig. 2: Exemplary transient WAXS signal recorded after 400 nm photoexcitation of aqueous I_3^- produced from pairs of azimuthally integrated laser on and laser-off images. The different time delays are color coded, the x-axis displays the scattering vector q, while the y-axis displays the intensity of the signal.

[1] V.-T. Pham et al., J. Am. Chem. Soc. **133**, 12740 (2011) (10.1021/ja203882y)
[2] J. A. Kloepfer et al., Chem. Phys. Lett. **298**, 120 (1998) (10.1016/S0009-2614(98)01210-X)
[3] K. H. Kim et al., Struct. Dyn. **1**, 011301 (2014) (10.1063/1.4865234)